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ON A ROLE OF THE MICROPOTENTIAL IN IONIC MASS TRANSFER CONTROLLED PROCESSES

By

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Among the problems encountered in description of macrokinetics of heterogeneous processes occurring at electrolyte solution—polarized medium interfaces the problem of taking into account the resistance offering by the diffuse double electrical layer to ionic mass transfer arises very often. For the present the majority of theoretical papers on analysis of the double layers effect on the rate of transport of ions from the bulk of the solution towards the electrode surface are based on the self-consistent electrical field approximation[1~7]. This field being quasi-external with respect to the transferred ions does not comprise the contribution of the interaction between the discrete charges of ions and the "electrostatic image" forces induced by the ions at the interphase boundary. Due to the presence of the interaction mentioned the actual local electrical field acting on any transferred ion (the potential of this field is generally accepted to be called the "micropotential") may differ rather appreciably from the averaged, self-consistent field. This difference is the cause of the existence of the "discreteness of charge effect". One of the most illustrative examples of manifestation of the discreteness of charge effect consists in the considerable divergence between the slope of the experimental curves characterizing the dependence of the adsorption potential drop at the metal-solution interface and the corresponding slope calculated in terms of the Gouy-Chapman-Stern theory[8]. The importance of consideration of the discreteness of charge effect in interpretation of results of electrochemical measurements was emphasized in literature[9~11]. Nevertheless a role of this effect in ionic mass transfer controlled processes remained non-clarified up to the present. The goal of this paper is a theoretical analysis of the effect of the "electrostatic image" forces on the rate of ionic mass transfer from the electrolyte solution to

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the charged metallic electrode surface.

The magnitude of the micropotential determining the local value of the electrostatic free energy of the transferred ions depends very strongly on the state of polarization of the solvent near the electrode surface and on the interaction between the ions and the charges induced at the electrode (*i.e.* the ion—"electrostatic image" interaction). For this reason in quantitative consideration of processes occurring within the double electrical layer an adequate choice of the model of the spatial distribution of the dielectric properties of the solvent in the vicinity of the electrode surface is of great importance. In papers[12,13], within the framework of the classical electrostatics a rigorous mathematical analysis of the micropotential distribution in dielectrically inhomogeneous and unisotropic media has been done. This analysis permits, in principle, to indicate one of the possible ways of the further progress in the field of the double layer theory and its application to non-equilibrium phenomena at charged interfaces. This way consists in generalization of the results of papers[12,13] where a single point charge in a pure solvent was treated on the case of a statistical system of point charges interacting with one another as well as with the electrical field of the polarization induced by these charges at the interphase. Partially such a generalization was accomplished[14~16] for the case of localization of a fixed ion within the Helmholtz layer with the inhomogeneous dielectric permittivity distribution inside the layer. This approach enabled the micropotential as a functional of the dielectric permittivity distribution to be calculated. In particular, in paper[16] the influence of the continuosly and monotonously varying dielectric permittivity of the Helmholtz layer on the micropotential magnitude was analyzed. It should be pointed out, however, that the approach mentioned is invalid for description of heterogeneous processes occurring in the double layer in cases when the process rate is limited, though partially, by the rates of diffusion and migration through the double layer. In such cases for calculation of the macroscopic rate of the process it is necessary to solve the problem of the micropotential in two regions with the essentially different charge distributions : in the diffuse layer where any fixed ion is surrounded by the ionic atmosphere formed by the statistical distribution of the remainder ions of the solution and in the Helmholtz layer where the charge density is determined entirely by the fixed ion. In both regions the micropotential magnitude depends on the particular form of the dielectric permittivity distribution near the electrode. A proper mathematical treatment of the problem of the micropotential in the diffuse double layer demands the use of a rather cumbersome formalism even within

the framework of the simplest model of the step-wise discontinuous dielectric permittivity distribution (with constant but different values in the Helmholtz and the diffuse layers). In this paper a very simple continuous dielectric permittivity distribution model will be used. Namely, it will be supposed that the permittivity $\varepsilon(x)$ is constant over the region I ($0<x<x^*$) inside the Helmholtz layer (the latter will be denoted as the region $0<x<d$ adjacent to the electrode surface $x=0$) and is a linear function of the distance x over the region II ($x^*<x<d$); inside the diffuse part of the double layer the value ε will be considered as homogeneously distributed and equal to the bulk value ε_0. Hence,

$$\varepsilon(x)=\begin{cases}\varepsilon_1=\text{const} & 0\leqslant x\leqslant x^* \quad \text{(region I)}\\ ax+b & x^*\leqslant x\leqslant d \quad \text{(region II)}\\ \varepsilon_0=\text{const} & d\leqslant x\leqslant\infty \quad \text{(region III)}\end{cases} \tag{1}$$

The values ε_0, ε_1, d and x^* are supposed to be known from experimental data, the parameters a and b being determined by the relationships

$$a=\frac{\varepsilon_0-\varepsilon_1}{d-x^*}, \qquad b=\frac{\varepsilon_1 d-\varepsilon_0 x^*}{d-x^*}.$$

It is unreasonable to consider more complex distributions $\varepsilon(x)$ than the one determined by Eq. (1). Qualitatively this function seems to represent the main features of the spatial inhomogeneity of the dielectric properties of the solvent in contact with the charged electrode, the current state of the theory does not describe this inhomogeneity quantitatively.

Consider the problem of the steady-state regime of transfer of ions having the charge ez_a and the local concentration $C_a(x)$ from the non-mixed solution to the planar charged metallic electrode surface (the potential of which, relative to the bulk of the solution, being denoted by ϕ_0) under conditions of the presence of the excess of the indifferent z-z-electrolyte in the solution. The bulk concentration of the latter will be denoted as $C_b^{(0)}$. If the solution is sufficiently diluted, *i.e.* the condition $\kappa^3 v\ll 1$ is fulfilled ($\kappa=(8\pi e^2 z^2 C_b^{(0)}/\varepsilon_0 kT)^{1/2}$ is the reciprocal Debye length, v being the average volume of the solution per an ion), it is possible to expand the non-equilibrium ion distribution functions into power series with respect to the parameter $\kappa^3 v$ and to obtain the closed equations for the first several terms of the expansion. As it was shown in paper[17] in the first approximation with respect to $\kappa^3 v$ the mass transfer equation takes the form

$$\frac{d^2 C_a}{dx^2}+\frac{1}{kT}\frac{d}{dx}C_a\frac{dW}{dx}=0. \tag{2}$$

Here $W=W(z_a, x)$ is the electrostatic free energy per one ion transferred. In the presence of the excess of the indifferent electrolyte in the solution this energy is independent of the local concentration C_a, so Eq. (2) can be easily integrated. If one supposes that the transferred ions participate in the infinitively fast electrochemical reaction at the electrode and if $x=x_0$ is the position of the effective plane where the reaction occurs, the solution of Eq. (2) is

$$C_a(x)=C_a^{(0)}\exp\left[-\frac{W(z_a, x)}{kT}\right]\left\{1-\frac{\int_x^{x_d}\exp\left[\frac{W(z_a, x')}{kT}\right]dx'}{\int_{x_0}^{x_d}\exp\left[\frac{W(z_a, x')}{kT}\right]dx'}\right\} \qquad (3)$$

where $C_a^{(0)}$ is the bulk concentration of the ions ez_a, $x=x_d=\kappa^{-1}$ is the outer boundary of the diffuse part of the double layer ($W=0$, $C_a=C_a^{(0)}$ at $x\geqslant x_d$). Eq. (3) determines the mass flux of the ions to the electrode surface.

$$j_a=D_a\left(\frac{dC_a}{dx}\right)_{x=x_0}=D_aC_a^{(0)}\left\{\int_{x_0}^{x_d}\exp\left[\frac{W(z_a, x)}{kT}\right]dx\right\}^{-1} \qquad (4)$$

Here D_a is the diffusion coefficient of the ions transferred.

Without taking into account the discreteness of charge effect the electrostatic free energy $W(z_a, x)$ would be determined by the expression

$$W(z_a, x)=W^*(z_a, x)=ez_a\phi(x) \qquad (5)$$

where $\phi(x)$ is the self-consistent field potential statisfying the system of equations

$$\frac{d^2\phi_1}{dx^2}=0 \qquad (0<x<x^*) \qquad (6)$$

$$\frac{d^2\phi_2}{dx^2}+\frac{d\ln\varepsilon}{dx}\frac{d\phi_2}{dx}=0 \qquad (x^*<x<d) \qquad (7)$$

$$\frac{d^2\phi_3}{dx^2}-\frac{8\pi ezC_b^{(0)}}{\varepsilon_0}\sinh\frac{ez\phi_3}{kT}=0 \qquad (d<x<x_d) \qquad (8)$$

with the boundary conditions

$$\begin{aligned}
&\phi_1=\phi_0 && \text{at} && x=0\,;\\
&\phi_1=\phi_2\,, && \frac{d\phi_1}{dx}=\frac{d\phi_2}{dx} && \text{at} && x=x^*\,;\\
&\phi_2=\phi_3\,, && \frac{d\phi_2}{dx}=\frac{d\phi_3}{dx} && \text{at} && x=d\,;\\
&\phi_3=0 && && \text{at} && x=x_d\,.
\end{aligned} \qquad (9)$$

Here and throughout the further developments the subscripts 1, 2 and 3 will be referred to functions of the coordinate x determined, correspondingly, in the regions I, II and III. It is easy to check up that the solution of Eqs. (6)~(8) is

$$\phi_1 = \phi_0 - \frac{2kT\varepsilon_0\kappa x}{ez\varepsilon_1}\sinh\frac{ez\phi_1}{2kT}$$

$$\phi_2 = \phi_0 - \frac{2kT\varepsilon_0\kappa x^*}{ez\varepsilon_1}\left(1+\frac{\varepsilon_1}{x^*}\int_{x^*}^{x}\frac{dx'}{\varepsilon(x')}\right)\sinh\left(\frac{ez\phi_1}{2kT}\right)$$

$$\phi_3 = \frac{2kT}{ez}\ln\left\{\frac{1+\exp\left[-\kappa(x-d)\right]\tanh\left(ez\phi_1/4kT\right)}{1-\exp\left[-\kappa(x-d)\right]\tanh\left(ez\phi_1/4kT\right)}\right\}$$

where ϕ_1 is the potential of the outer Helmholtz plane ($x=d$) related to the electrode potential ϕ_0 by the relationship

$$\phi_0 = \phi_1 + \frac{2kT\varepsilon_0\kappa x^*}{ez\varepsilon_1}\left(1+\frac{\varepsilon_1}{x^*}\int_{x^*}^{d}\frac{dx'}{\varepsilon(x')}\right)\sinh\left(\frac{ez\phi_1}{2kT}\right).$$

The expressions for the potential presented above permit to calculate the ilmiting diffusion flux, j_a^*, in the absence of the discreteness of charge effect:

$$j_{a_1}^* = D_a C_a^{(0)}\kappa\left\{\kappa\int_{x_0}^{x^*}\exp\left(\frac{ez_a\phi_1}{kT}\right)dx+\kappa\int_{x^*}^{d}\exp\left(\frac{ez_a\phi_2}{kT}\right)dx+\Lambda(d)\right\}^{-1} \tag{10}$$

$$j_{a_2}^* = D_a C_a^{(0)}\kappa\left\{\kappa\int_{x_0}^{d}\exp\left(\frac{ez_a\phi_2}{kT}\right)dx+\Lambda(d)\right\}^{-1} \tag{11}$$

$$j_{a_3}^* = D_a C_a^{(0)}\kappa\Lambda^{-1}(x_0) \tag{12}$$

where

$$\Lambda(x) = 1+2\sum_{p=0}^{m-1}\frac{1}{2p+1}\left[\left(\frac{1+\exp\left[-\kappa(x-d)\right]\tanh\left(ez\phi_1/4kT\right)}{1-\exp\left[-\kappa(x-d)\right]\tanh\left(ez\phi_1/4kT\right)}\right)^{2p+1}-1\right] \tag{13}$$

Eq. (13) in which the notation $m=|z_a|/z$ is introduced is valid provided the valency ratio of the ions responsible for interphase mass transfer and the indifferent electrolyte ions equals to some integer (either positive or negative).

In order to evaluate the contribution to the ionic mass transfer rate due to the discreteness of charge effect it is necessary to take into account the explicit form of interaction between the transferred ion and the ambient ionic atmosphere (the latter is distorted, compard with the spherically symmetrical Debye atmosphere, by the presence of the interphase layer with

spatially inhomogeneous dielectric properties). It was shown[17] that in the presence of the ion-atmosphere interaction the energy $W(z_a, x)$ was determined by the expression

$$W(z_a, x) = ez_a\phi(x) + \chi(z_a, x)$$

where the function $\chi(z_a, x)$ represented the interaction energy between the given ion (with the charge ez_a) and the "electrostatic image" forces induced at the interphase by the given ion as well as by all of the rest ions in the solution. The explicit functional form of the energy $\chi(z_a, x)$ changes depending on the location of the reaction plane $x_a = x_0$ inside the double layer. It can be shown[18] that this energy is associated with the Green function, G, of the corresponding double layer problem by means of the following relation:

$$\chi(z_a, x) = ez_a \lim_{\vec{r}\to\vec{r}'} \int_0^1 \left\{ \left[G(\vec{r}, \vec{r}', \xi z_a) - G^*(\vec{r}, \vec{r}', \xi z_a) - \phi(x') \right] - \right.$$

$$\left. - \lim_{x'\to\infty} \left[G(\vec{r}, \vec{r}', \xi z_a) - \frac{\xi e z_a}{\varepsilon_0 |\vec{r} - \vec{r}'|} \right] \right\} d\xi \,. \qquad (14)$$

Here $G^*(\vec{r}, \vec{r}', z_a)$ is the Green function of the purely electrostatic problem for the given dielectrically inhomogeneous medium. This function obeys the equation

$$\mathrm{div}\,(\varepsilon \nabla G^*) = -4\pi e z_a \delta(\vec{r} - \vec{r}')$$

with respect to the coordinate $\vec{r}$ and the boundary conditions

$$G^* \to 0 \qquad \text{at} \qquad |\vec{r} - \vec{r}'| \to \infty \,;$$

$$\frac{\partial G^*}{\partial |\vec{r}|} \to - \frac{e z_a}{\varepsilon(\bar{r}) |\vec{r} - \vec{r}'|^2} \qquad \text{at} \qquad |\vec{r} - \vec{r}'| \to 0 \,.$$

$\delta(\vec{r} - \vec{r}')$ being the Dirac delta-function. For the dielectrical inhomogeneity described by the distribution (1) one can obtain the following expression for G^* in the region II (in other two regions G^* must be a purely Coulombic function with a corresponding dielectric permittivity):

$$G^*(\vec{r}, \vec{r}', z_a) = \frac{4ez_a}{a} \int_0^\infty \Phi^*(x, x', \lambda)\, J_0\left(\lambda \sqrt{(y - y')^2 + (z - z')^2} \right) \lambda d\lambda \,,$$

$$\Phi^*(x, x', \lambda) = \begin{cases} I_0\left(\frac{2\lambda}{a} \sqrt{\varepsilon_0 (ax' + b)} \right) K_0\left(\frac{2\lambda}{a} \sqrt{\varepsilon_0 (ax + b)} \right) & x \geqslant x' \,; \\ I_0\left(\frac{2\lambda}{a} \sqrt{\varepsilon_0 (ax + b)} \right) K_0\left(\frac{2\lambda}{a} \sqrt{\varepsilon_0 (ax' + b)} \right) & x \leqslant x' \,, \end{cases}$$

where J_0 is the Bessel function of the first kind, I_0 and K_0 are the Bessel

functions of the second kind. It can be shown that in the limiting case of the homogeneous dielectric permittivity distribution ($\varepsilon_0 \to \varepsilon_1$, $x^* \to 0$) the above expression leads to the well kown Coulombic function:

$$G^*(\vec{r}, \vec{r}', z_a) = \frac{ez_a}{\varepsilon_0 |\vec{r}-\vec{r}'|} =$$

$$= \frac{ez_a}{\varepsilon_0} \int_0^\infty \exp\left[-\lambda|x-x'|\right] J_0\left(\lambda\sqrt{(y-y')^2+(z-z')^2}\right) d\lambda$$

In accordance with the chosen model of dielectric inhomogeneity the Green function $G(\vec{r}, \vec{r}', z_a)$ must satisfy one of the following three systems of equations:

$$\left.\begin{aligned} &\operatorname{div} \nabla G_1^{(1)} = -\frac{4\pi e z_a}{\varepsilon_1} \delta(\vec{r}-\vec{r}') \\ &\operatorname{div}\left\{(ax+b)\nabla G_2^{(1)}\right\} = 0 \\ &\operatorname{div} \nabla G_3^{(1)} - \frac{8\pi e z C_b^{(0)}}{\varepsilon_0} \sinh\left(\frac{ezG_3^{(1)}}{kT}\right) = 0 \end{aligned}\right\} 0 \leqslant x' \leqslant x^* \qquad (15)$$

$$\left.\begin{aligned} &\operatorname{div} \nabla G_1^{(2)} = 0 \\ &\operatorname{div}\left\{(ax+b)\nabla G_2^{(2)}\right\} = -4\pi e z_a \delta(\vec{r}-\vec{r}') \\ &\operatorname{div} \nabla G_3^{(2)} - \frac{8\pi e z C_b^{(0)}}{\varepsilon_0} \sinh\left(\frac{ezG_3^{(2)}}{kT}\right) = 0 \end{aligned}\right\} x^* \leqslant x' \leqslant d \qquad (16)$$

$$\left.\begin{aligned} &\operatorname{div} \nabla G_1^{(3)} = 0 \\ &\operatorname{div}\left\{(ax+b)\nabla G_2^{(3)}\right\} = 0 \\ &\operatorname{div} \nabla G^{(3)} - \frac{8\pi e z C_b^{(0)}}{\varepsilon_0} \sinh\left(\frac{ezG_3^{(3)}}{kT}\right) = -\frac{4\pi e z_a}{\varepsilon_0} \delta(\vec{r}-\vec{r}') \end{aligned}\right\} d \leqslant x' \leqslant x_d \qquad (17)$$

depending on within which of the regions, I, II or III, the "test" point charge ez_a is located. In systems (15)~(17) the index "i" of the functions $G_k^{(i)}$ indicates belonging of the coordinate x' to the corresponding region (I, II or III), the subscript "k" is used for notation of the region of localization of the coordinate x. Thus, if *e.g.*, the coordinate x is located within the region I, the corresponding energy of interaction with the ionic atmosphere should be denoted as $\chi_1(z_a, x)$; in this case for calculation of the value $\chi_1(z_a, x)$ one must use Eq. (14) with the function $G_1^{(1)}$ which is a solution of the system (15) and the Coulombic function $G_1^* = \xi e z_a/\varepsilon_1 |\vec{r}-\vec{r}'|$. In calculating the energy $\chi_3(z_a, x)$ one must insert the function $G_3^{(3)}$ satisfying

the system (17) and the function $G_3^* = \xi e z_a/\varepsilon_0|\vec{r}-\vec{r}'|$ into Eq. (14). The boundary conditions for the functions $G_k^{(i)}$ with respect to the coordinate x coincide with the boundary conditions (9).

Solution of any of the system (15)~(17) can be obtained by the method of "matching of asymptotic expansions" known from fluid mechanics of viscous flows[19]. Applicability of this method to problems of statistical mechanics of systems with Coulombic interaction was demonstrated[20]. In the present paper the condition of smallness of the parameter $\zeta=\kappa d$ was used (for aqueous solution of 1-1 valent electrolytes at $d\approx 3$ Å and $C_b^{(0)}\lesssim 10^{-2}$ moles per litre the value ζ does not exceed 0.1) and asymptotic expressions for the functions $G_k^{(i)}$ corresponding to small (compared to x_a) and large (compared to d) distances x were found. Having carried out the standard procedure of "matching" the expansions and having inserted the solution therein obtained into Eq. (14) the author arrived at the analytical expressions for the energies $\chi_k(z_a, x)$ $(k=1, 2, 3)$. Using these expressions and Eq. (4) the values of the limiting diffusion flux $j_{ak}(k=1, 2, 3)$ were calculated for various values of the parameters ε_1 and x^* characterizing dielectrical inhomogeneity of the double layer as well as for different positions of the plane $x=x_0$ where interphase mass transfer occurs. In Tables 1~3 calculated values of the dimensionless mass fluxes $J_a=j_a(D_a C_a^{(0)}\kappa)^{-1}$ are presented as functions of the electrode potential ϕ_0. For the limiting case of the "dielectrical step" situation $(x^*=d)$ corresponding to the classical model of the Helmholtz layer with a constant (but different from the bulk one) value of the dielectric permittivity, in Tables 1 and 2 the calculated values are compared with that determined by the expression (12) which does not take into account the discreteness of charge contribution. All the values in

TABLE 1. Dimensionless mass fluexes $J_{a3}=j_{a3}(D_a C_a^{(0)}\kappa)^{-1}$ and $J_{a3}^*=j_{a3}^*(D_a C_a^{(0)}\kappa)^{-1}$ corresponding to the case of discharge of divalent ions $(|z_a|=2)$ at a similarly charged metallic surface as functions of the electrode potential and the effective dielectric permittivity of the Helmooltz layer $(z=1,\ c_b^{(0)}=10^{-3}\,\mathrm{M},\ d=3.3\,\text{Å},\ x_0=6.6\,\text{Å},\ \beta=\varepsilon_1/\varepsilon_0,\ x^*=d)$.

ϕ_0, volts	$J_{a3}\cdot 10^5$		$J_{a3}^*\cdot 10^5$	
	$\beta=0.1$	$\beta=0.2$	$\beta=0.1$	$\beta=0.2$
2.0	4.43	6.16	1.09	0.975
4.0	4.02	5.82	0.873	0.764
6.0	3.86	5.70	0.758	0.714
8.0	3.82	5.67	0.727	0.698

TABLE 2. Dimensionless mass fluxes J_{a3} and J^*_{a3} for the case of discharge of trivalent ions ($|z_a|=3$) at a similarly charged electrode ($z=1$, $c_b^{(0)}=1.2.10^{-2}$M, $d=3$Å, $x_0=5$Å, $\beta=\varepsilon_1/\varepsilon_0$, $x^*=d$).

ϕ_0, volts	$J_{a3}\cdot 10^5$		$J^*_{a3}\cdot 10^5$	
	$\beta=0.1$	$\beta=0.2$	$\beta=0.1$	$\beta=0.2$
0.2	298	381	277	36.9
0.3	54.9	66.8	36.6	5.16
0.4	20.1	23.2	9.57	1.55
0.5	11.7	13.3	4.34	0.612
0.6	7.44	8.40	2.26	0.288
0.7	4.49	4.75	1.15	0.202

TABLE 3. Dependence of the dimensionless flux $J_{a2}=j_{a2}(D_a C_a^{(0)}\kappa)^{-1}$ on the electrode potential ϕ_0 at different concentrations of a 1-1-valent indifferent electrolyte ($x^*=0$, $x_0=2$ Å, $d=5$ Å, $\beta=\varepsilon_1/\varepsilon_0$, $|z_a|=2$).

ϕ_0, volts	$C_b^{(0)}=3.10^{-3}$ M		$C_b^{(0)}=7.10^{-3}$ M		$C_b^{(0)}=10^{-2}$ M	
	$\beta=0.05$	$\beta=0.2$	$\beta=0.05$	$\beta=0.2$	$\beta=0.05$	$\beta=0.2$
0.6	2.59	1.93	3.16	2.39	3.37	2.43
0.7	1.95	1.41	2.53	1.89	2.56	1.98
0.8	1.50	1.11	1.84	1.39	1.96	1.41
1.0	0.952	0.730	1.16	0.926	1.18	0.943
1.3	0.476	0.410	0.585	0.518	0.610	0.535

Tables 1~2 correspond to the reaction plane ($x=x_r$) located in the diffuse part of the double layer. It is seen that the discreteness of charge effect tends to increase the mass transfer rate, the degree of this augmentation being higher when the difference between the dielectric permittivities of the Helmholtz layer and the bulk of the solution is smaller (the parameter β represents the ratio $\varepsilon_1/\varepsilon_0$). The latter circumstance is connected with the obvious physical fact that the "own electrostatic image" forces induced by an ion on a metallic electrode and attracting this ion to the electrode become weaker in the presence of a "dielectric interlayer" whose role is played by the Helmholtz layer. According to the results obtained the effect of attenuation of the "electrostatic image" forces is more profound for bigger ion charges and for smaller effective dielectric permittivities of

the Helmholtz layer. The character of interaction between an ion and an induced polarization of the Helmholtz layer is responsible for one more intrinsic feature of the results presented in the tables: at sufficiently high electrode potentials higher mass transfer rates correspond to larger values of the parameter β (if one does not take into account the discreteness of charge effect lower fluxes must correspond to larger β as it follows from the last two columns of each of the Tables 1 and 2).

Analysis of the effect of the "electrostatic image" forces on ionic mass transfer was done also for the case of continuous variation of the dielectric permittivity through the double layer. Calculations were carried out for the case of penetration of the reacting ions into the Helmholtz layer ($x_0<d$). In order to illustrate the influence of dielectric inhomogeneity of the double layer the values of the limiting diffusion flux were calculated for the situation when divalent ions discharge from a solution containing an excess of an indifferent 1-1-valent electrolyte at the surface of a similarly charged electrode. Effects of the indifferent electrolyte concentration (within the range from 3.10^{-3} to 10^{-2} moles per litre) and the degree of dielectric inhomogeneity (which can be characterized by the parameters $\alpha=x^*/d$ and $\beta=\varepsilon_1/\varepsilon_0$) were investigated. In Table 3 the results of calculation for the case $\alpha=0$ are presented. As one can see from the table in the case of penetration of ions into Helmholtz layer the mass transfer resistance of the double layer is being reduced with increasing degree of dielectric inhomogeneity (*i.e.* with decreasing parameter β) and with the elevation of the indifferent electrolyte concentration (*i.e.* with the decrease of the effective thickness of the diffuse part of the double layer). It should be noted that in the case considered the dependence of the flux J_a on the effective double layer thickness x_d does not show any qualitative difference from the analogous dependence for the case of a heterogeneous reaction occurring outside the Helmholtz layer (see Tables 1 and 2). However, the dependence of J_a on β in the two above mentioned cases show directly opposite behavior. Namely, at $x_0>d$ the flux J_a decreases with decreasing parameter β whereas at $x_0<d$ a decrease of the parameter β results in a reduction of the double layer resistance to ionic mass transfer. The physical cause of this difference consists in the fact that the ions located in the Helmholtz layer are subjected to the attraction force due to the "own electrostatic imaging" in the metal surface whereas within the diffuse part of the double layer the resulting action of the "image" forces appears to be repulsion of ions from the interphase boundary. It is worth-while to point out that without taking into account the discreteness of charge effect

(*i.e.* under the formal condition $\chi(z_a, x)\equiv 0$) the calculated values J_a would appear to be significantly (to the factor ao 2–3) greater compared with the corresponding values presented in Table 3. This difference is caused by the opposite signs of the energies of interaction of ions with "own electrostatic images" and with the external field exerted by the electronic charge of the metal.

The analysis carried out in this paper evidences therefore of a very important role of the discreteness of charge effect in processes involving ionic mass transfer in electrolyte solutions.

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